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WATER VAPOR DIFFUSION THROUGH PROTECTIVE COATINGS. PART I.

A METHOD OF MEASURING WATER VAPOR PERMEABILITY OF COATING FILMS

BY RADIOISOTOPE TRACER TECHNIQUE AND ITS APPLICATION

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NAVAL CIVIL ENGINEERING LABORATORY
Port Hueneme, California

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ABSTRACT

A method of measuring the permeability constant and the diffusion rate of water vapor through a polymer film by the radiochemical method is elaborated. It demonstrates that the radiochemical method, as compared to the ASTM Standard Method, is precise, sensitive and rapid. The radiochemical method is also useful in the investigation of other parameters which influence permeability of water vapor.

INTRODUCTION

The Naval Facilities Engineering Command is responsible for the operation and maintenance of the many structures throughout the Naval Shore Establishment. These structures are subject to corrosion and deterioration from their natural environment and must be protected to minimize this deterioration and resultant costly repairs.

It is a well established[1,2,3,4,5] and recognized fact that metal corrosion is electrochemical in nature, and no further discussion is necessary on this basic subject. Since practically all electrochemical or common corrosion processes require the presence of water or water vapor, it should be possible to prevent or reduce corrosion by isolating metallic surfaces from water or water vapor.

Painting is the most widely used method for minimizing corrosion of large surface areas because of the simplicity of application and the low initial cost. Paints, however, have inherent deficiencies that allow water or other corrosive materials to penetrate the film to the substrate in varying degrees and eventually affect the protection of coatings. Hence a detailed study of the mechanism of water vapor permeation through organic coatings should help in understanding the limitations of these paint films and, hopefully, will suggest ways and means by which they may be improved.

BACKGROUND

The permeability of coatings to moisture has been studied by many workers,[6,7,8,9,10,11] but their studies have been very limited and the accuracy of data on water vapor transmission is much less than desired. This situation is caused by the difficulty associated with measuring accurately the quantity of water vapor diffusing through a film. The amount is usually too minute to be accurately measured by chemical means, and is in a form which is not determinable by the usual analytical methods.

In the method for measuring water vapor transmission through a film given in ASTM Standard D1653-62T, the loss of weight of water passing through a sample film is determined under a specific set of conditions. This method will not afford results in a reasonably short time because the weight of water vapor passed is too small to be measured accurately. This method is neither as sensitive nor as accurate as one desires and so is used only for the preliminary determination of water vapor transmission. It also lacks versatility in its application, in that the method does not provide for controlled experiments

in which the effects of changing temperature, vapor pressure, etc., can be used to characterize the mechanisms of water vapor diffusion.

This study was undertaken to develop an improved method for measuring vapor diffusion through films as applied to paint, by using tritiated water as a tracer. With such a technique, the permeability coefficient of widely differing materials could be measured with high speed and accuracy. Systems have been proposed[14,15] and investigated,[16,17,18] in which radioisotope tracer techniques are used to measure water vapor and ionic diffusion through protective films.

This report describes the development of a sensitive and versatile radiometric method to measure water vapor permeability through organic membranes and its application to an investigation of the basic factors which may play an important role in water vapor transmission.

THEORY OF PERMEATION

The mechanism of vapor diffusion through an organic membrane is not a simple diffusion process as in a porous material. It is a generally accepted theory[6,12] that the permeation process occurs in three stages: (1) condensation and dissolving of water vapor in one side of the film, (2) diffusion through the film, (3) evaporation from the other side. Because of this dual transfer mechanism of solution and diffusion, the permeability of the vapor is a product of its diffusion coefficient (D) through the membrane and its solubility (S) in the membrane. It is mathematically expressed as[6,12]

$$P_r = D \, S \qquad (1)$$

Where

P_r = Permeability in $gm\text{-}cm/cm^2/cmHg/hr$,

D = Diffusion Coefficient in cm^2/hr,

S = Solubility of penetrant in $gm/cm^3/cmHg$.

The driving force for water vapor diffusion through the organic membrane is the vapor pressure difference between its two faces. The amount of water vapor (Q) diffusing through a given membrane at a given temperature is dependent upon the effective area (A), the thickness (d), the vapor pressure differential between the faces of the membrane (Δp), and the time (t), according to the following one-dimensional steady state equation[6,13] from Fick's Law;

$$Q = \frac{P_r}{d} \cdot A \cdot t \cdot \Delta p \qquad (2)$$

The permeability (P_r) which characterizes the water vapor transmission resistance of the membrane under consideration is dependent upon the nature of both the membrane and the permeating vapor. It is interesting to note that this permeability equation (2) is completely analogous[12] to the basic heat conduction equation:

$$Q = \frac{K}{d} . A . t . \Delta p \qquad (3)$$

in which permeability (P_r) is analogous to conductivity (K), and the partial pressure difference (Δp), is analogous to the temperature difference (ΔT).

The dependence of the amount of water vapor (Q) diffusing through the membrane upon the time (t), and area (A) in Equation (2) seems obvious. The validity of the linear dependence of amount of diffusing water vapor (Q) on vapor pressure and inverse linear dependence on membrane thickness will be examined. The validity of the independence of permeability (P_r), from varied vapor pressures, thicknesses and temperatures of film will also be investigated.

RADIOCHEMICAL EXPERIMENTAL METHOD

Apparatus

Diffusion Cell: A detailed diagram of the present design of the diffusion cell is shown in Figure 1. The diffusion cell is made of Plexiglas (A) and Pyrex glass tubing (B). Each half of the diffusion cell consists of a water mantle (C) and an exposure chamber (D). The water mantles (C) maintain the desired temperature in the chambers and the sample membrane (E) during the experiments. The sample membrane is placed between two fine copper gauzes (F). An O ring (G) and a rubber gasket (H) are used for sealing the two halves of the diffusion cell. When the cell is assembled, the exposed portion of the sample membrane is 20 cm^2 in area. The copper gauzes give even support to the sample membrane while protecting it from damage which might occur by a sudden change in pressure between the two chambers. The lower chamber is provided with a thermocouple probe (I) which enables an experimenter to monitor the temperature of the sample membrane directly rather than relying on the water mantle temperature. Screw (J) is tightened with moderate fingertight force to secure a high-vacuum seal.

Vacuum System: In order to measure the permeation rate through a sample membrane, a known constant pressure of water vapor is maintained on the surface of the sample membrane by means of a vacuum system represented diagrammatically in Figure 2. The vacuum system, including the glass tubing and stopcocks is made of high-vacuum grade Pyrex glass except for the previously described diffusion cell (1,2). The vessel

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(3) which contains tritiated water is connected, through a T-shape
stopcock (4), with the lower half of the diffusion cell (1) (separated
from the upper half (2) by the sample membrane), and with an arm of
the manometer (6) through T-shape stopcock (5). The other arm of the
manometer is connected through a T-shape stopcock (16) to the upper
half of the diffusion cell (2). The manometer thus provides direct
reading of vapor pressure differential between the two faces of the
sample membrane rather than the assumed vapor pressure on one surface
based on the temperature of the tritiated water in the vessel (3).
This manometer is also equipped with a vapor pressure controlling device
(7) which regulates the temperature of the tritiated water in the vessel.

The desired temperature of the sample membrane, the diffusion cell,
and the entire vacuum system is maintained constant throughout an experi-
ment by the water mantle and the heating element (18), partially shown
in Figure 2, which is wound over all the glass tubing. This temperature
regulating device prevents condensation of tritiated water vapor within
the Pyrex glass tubing by maintaining the temperature above the dew
point at all times.

The vacuum system is designed in such a way that the diffusion
cell, the mercury manometer or other elements can be disconnected from
the assembly by a number of controlling stopcocks as can be seen in
Figure 2.

Method of Determining Permeability

The unpigmented films described in this report were prepared by
the method described by Drisko and Matsui.[19] Films that were not of
uniform thickness (deviation of more than ± 0.2 mil) and not free of
air bubbles and other flaws which might affect experimental results
were rejected. Film thickness were measured with a micrometer.

A sample membrane was placed in the diffusion cell and the cell
(1,2) was mounted on the vacuum system as shown in Figure 2. The
tritiated water (approximately 10 to 15 ml) of known activity (approxi-
mately 15 microcuries (μc) per ml) in the vessel (3) was frozen by a
mixture of dry ice and cellosolve, and the vessel was evacuated several
times to remove dissolved gas prior to the experiments. The cold trap
and the Drierite (14) are connected in series before the vacuum pump
to remove any residual tritiated water vapor which may be present in
the vacuum system during the evacuation. Stopcock (4) was then closed
with respect to vessel (3). The same operation was followed with
the absolute alcohol in tube (8) and then stopcock (9) was closed to
avoid reabsorption of gas from the atmosphere until the experiment
begins.

The whole vacuum system, with stopcocks (4) and (9) closed, was
then evacuated for 15 minutes, or longer, until the pressure of the
vacuum system was reduced to less than 1.0 mmHg as indicated by the
vacuum gage (13). The stopcocks of the receiving tubes (10, 11, and 12)

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were then closed and one of the receiving tubes (10) was dipped in a Dewar flask containing dry ice and cellosolve mixture.

Stopcock (15) was then closed and T-shape stopcock (5) was turned with the foot of the "T" toward stopcock (15) to cut off the pumping action from the experimental system and to connect each half of the diffusion cell (1,2) separated by the sample membrane, to an arm of the manometer (6). The vapor pressure controlling device was later adjusted to obtain the desired vapor pressure difference.

Tritiated water vapor from the vessel was admitted into the manometer through T-shape stopcock (4). As soon as the desired vapor pressure was obtained as indicated by the manometer, tritiated water vapor was admitted into lower half of the diffusion cell through the T-shape stopcock (4). Admission of the tritiated water vapor into the lower half of the cell is the initial moment (t = 0) of the experiment.

The stopcock for receiving tube (10), which was immersed in coolant, was then opened to condense and freeze out any tritiated water vapor which passed through the sample membrane. Freezing of the receiving tube ensured a constant pressure difference between the two faces of the sample membrane, since any vapor which passes through the membrane will be frozen out in the receiving tube.

After a predetermined length of time, approximately one to two hours, the vessel (3) was closed from the rest of the system by turning stopcock (4), and that time was recorded as the end of the experiment.

Vapor from the warmed absolute alcohol (approximately 40°C) in tube (8) was then released into the upper half (2) of the diffusion cell to purge it of any residual tritiated water vapor which was carried to and frozen out in receiving tube (10). The stopcock for the receiving tube (10) was closed after repeating the above purging procedure several times.

Method of Counting and Calculation

The tritiated water vapor condensed by the preceding procedure emits extremely soft β-radiation. A liquid scintillation spectrometer is most suitable for counting such a low energy beta emitter.

A most widely used scintillation solution, and the one used in these studies, is a mixture of "PPO", 2,5-diphenyloxazole, and "POPOP", p-bis-(2-5-phenyloxazolyl)-benzene, dissolved in toluene. This scintillation solution is commercially available.

The receiving tube (10), which contains the condensed tritiated water vapor, was then removed from the vacuum system and diluted with 1 ml of absolute alcohol. The absolute alcohol was added to make the liquid sample miscible with the scintillation solution. The sample diluted with alcohol was then transferred into a counting vial and diluted to its full volume (approximately 20 ml) with the scintillation solution.

The amount of the tritiated water vapor diffused through the sample membrane was used to calculate the diffusion rate, R, in

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mg/cm^2/hr and permeability constant, P_r, for the membrane in mg-mm/cm^2/ hr/cmHg by mean of the following formulas:

$$\text{Diffusion rate (R)} = \frac{N \cdot 100}{a \cdot A \cdot t \cdot k} \qquad (4)$$

$$\text{Permeability Constant } (P_r) = \frac{N \cdot d \cdot 100}{a \cdot k \cdot A \cdot t \cdot \Delta p} \qquad (5)$$

where

N = Rate in counts per minute

a = Specific activity of tritiated water, counts per min/mg

A = Effective area of sample membrane, cm^2

t = Exposed time, hours

k = Efficiency of scintillation counter, %

d = Thickness of sample membrane, mm

Δp = Vapor pressure difference between the two faces of the sample membrane, cmHg

In order to reduce the random error of counting to less than 1% at the 95% probability level, each sample is counted to register 40,000 or more counts at each measurement. The specific activity (a) of the tritiated water in the vessel is selected so as to give a required minimum count (40,000 plus) within a reasonable time (approximately 10-20 minutes). For highly impermeable membranes, tritiated water of higher activity should be used. Because of the high activity of the tritiated water, background activity need not be considered.

Counting efficiency (k) of the liquid scintillation counter is determined by applying the channel ratio method[20] described by E. T. Buch.

Since a steady rate of diffusion was not immediately attained during the experiment, a collection of condensates was repeated until the scintillation counts indicated that a diffusion rate plateau had been reached. A minimum of five samples was collected for analysis after a steady rate of diffusion was attained.

Processing of the results of the above procedure is greatly simplified by use of computer techniques. The liquid scintillation spectrometer can be loaded with up to 100 samples and each sample counted as many times as desired. The number of counts from each channel is

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automatically put on punch cards. These punched cards are fed into the computer along with other essential data. The computer will compute and print out counting rate, channel ratio, counting efficiency, diffusion rate, and the permeability constant of each sample in tabular form. The computer program together with input and output data is shown in Appendix A.

LABORATORY RESULTS

Reliability of Counting Data

The reliability of measured values obtained by the above radio-chemical method was determined by taking the count of each sample five times as shown in Table 1. The results show that the random count error of the above system is less than 1% per each measurement. It also indicates that the counting system is precise to a high degree, as long as each count is more than the required 40,000. However, it is preferable to take the count of each sample more than once since faulty operation or malfunctioning of instruments would not be dis-covered by a single counting.

Precision of Radiochemical Method

An alkyd resin was obtained from a local paint manufacturer and unpigmented films of several thicknesses were prepared as previously described.

Each prepared film was placed in the diffusion cell and exposed to the tritiated water vapor. The vapor pressure difference and temperature of the sample film were maintained at 20 mmHg and 30°C, respectively, throughout the experiment. The exposure times were varied from 50 minutes to 180 minutes for each sample film. The scintillation count of each sample was read and the diffusion rate determined as previously described. A minimum of five condensates was collected for each film after a state of steady vapor flow rate was attained.

The results for the water vapor diffusion rates are given in Table 2. The coefficients of variation were 4.02, 2.67, 7.50 and 3.79% at film thicknesses of 0.9, 1.9, 2.7 and 3.5 mils, respectively.

The precision of this radiochemical method was evaluated by comparing it with the precision obtained by the ASTM Standard method (D1653-62). The ASTM Standard Method uses a permeability cup which consists of two parts, - a shallow flanged cup and a flat ring matching the flange on the cup. Water is poured into the cup and the film under test is held tightly between the cup and ring by means of clamps.

The cup, so assembled, was placed in a dessicator and weighed each 24 hours for a period of one week. Phosphorous pentoxide was used as the dessicant. The dessicator was placed in a well ventilated room where the temperature was maintained between 70° to 85° F. The

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diffusion rate of water vapor passing through the film was determined from the weight loss rate.

The amount of moisture diffusing through a film is affected by the film thickness, as stated previously in formula (2). Since it is very difficult, if not impossible, to reproduce films with exactly the same thicknesses, the films used in the ASTM Standard Method were first used in the radiochemical method.

The diffusion rates obtained by the above ASTM Standard method are given in Table 3. The coefficients of variation were 8.86, 8.34, 8.56, and 59.66 at film thicknesses of 0.9, 1.9, 2.7 and 3.5 mils respectively, which are considerably larger than the coefficients of variation obtained by the radiochemical method. These larger values of the coefficients of variation were obtained even though the weight loss incurred in the first 24 hours period was excluded from the calculations because the water vapor diffusion rate did not attain a steady state of flow during that period.

The greater precision of the radiochemical method was determined statistically by the F-test. The F-test is a statistical measure used to compare the precision of two sets of measurements by taking the ratio of two variances. When the ratio of the variances (F-ratio) exceeds the critical value of F, which is obtained from the statistical table F, it implies that there is indeed a significant difference in the precision between the two systems. The critical value of significance, F, at the 99% and 99.9% levels are 3.37 and 5.30 respectively. The F-ratio obtained, 19.78, greatly exceeds the above two critical values. This indicates a very highly significant improvement in precision by the radiochemical method over that obtained by the ASTM Standard Method.

Summary of the Laboratory Results

Reliability of the above counting system was very good, and the random error of the counting system was well below 1% as shown in Table 1.

The sensitivity of the above counting system can be increased to measure down to 1 microgram (1×10^{-6} gm), whereas the analytical balance used in the ASTM Standard Method is accurate to 0.2 mg (200×10^{-6} gm). However, the precision of the diffusion system used in the radiochemical method as a whole is approximately ± 10 microgram (μg) at the 95% confidence level as shown in Table 2.

The diffusion rate, once a steady state of flow is attained, can be measured in a shorter time (1~2 hours) over one day whereas the ASTM Standard method required readings at 24 hour intervals over one week. Shorter intervals between readings by the radiochemical method is possible because of the almost instantaneous establishment of a vapor pressure gradient between the two surfaces of the sample membrane in the vacuum system, whereas, it may take several hours before a steady state pressure gradient can be established by the ASTM Standard Method.

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Statistical analysis indicated that the greater precision obtained by the radiochemical method was very highly significant over the precision obtained by the ASTM Standard Method.

Precisely monitorable vapor pressure differentials and temperatures with the radiochemical apparatus provide the means of examining the effects of vapor pressure and temperature separately on the permeability of the films, whereas it is not possible to monitor temperature without affecting vapor pressure by the ASTM Standard Method.

Since the tritiated water emits very soft β-radiation and only a small amount (approximately 150 μc per month) was used, elaborate safety precuations were not necessary. The U. S. Atomic Energy Commission (AEC) does not require a license for a package of tritiated water whose activity is less than 250 μc. A total of ten license-exempt quantities of tritium may be possessed at any one time. However, experimenters using radioisotopes may be subjected to institutional and local regulations in addition to AEC regulations.

APPLICATION OF RADIOCHEMICAL METHOD TO MOISTURE PERMEABILITY RESEARCH

Effect of Thickness

Equation 2 states that the amount of water (Q) diffusing through a permeable membrane at a given temperature is inversely proportional to thickness (d) and that the permeability constant (P_r) is independent of thickness (d). This inverse linear dependence of (Q) on thickness (d) was studied by testing a series of unpigmented films (alkyd TT-R-266 Type II and epoxy-polyamide cured) of different thicknesses. The films were prepared, and the diffusion rates and permeability constants (P_r) determined as described earlier. All sample films were subjected to a vapor pressure difference (Δp) of 2.0 cmHg at a temperature of 30° C during the measurements.

The rate of the moisture diffusing through the membrane increased inversely with the film thickness (d) in both type as shown in Table 4. The data obtained from samples less than 1 mil in thickness were not reliable, no doubt because of difficulty in preparing such thin films without pin holes or other defects. Since only two generic types of films, alkyd and epoxy, were tested, it is not established here whether all other types of films would behave similarly, but it is a reasonable assumption that they would differ only in degree as suggested in Figure 3.

The average permeability constants of the alkyd and of the epoxy films were 4.196 ± 0.200 and 1.000 ± 0.077 μg/mm/cm²/hr/cmHg respectively at the 95% confidence limit. It means that 19 times out of 20 the average permeability constant (P_r) will lie within the above range.

However, data in Table 4 show that the permeability constants (P_r) of the alkyd films fluctuated more than did those of the epoxy films. If permeability constant (P_r) is independent of thickness, then the

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plot of the diffusion rate versus 1/d (inverse thickness) should be a
straight line passing through the origin with a slope of $P_r(A \cdot \Delta p)$,
because area (A), vapor pressure difference (Δp), and temperature were
maintained constant during the experiment. The plots of diffusion rate
for progressively thinner alkyd films deviated from the expected straight
line, determined by step-wise linear regression analysis (STRAP), while
plots of diffusion rate for the epoxy films were as expected a straight
line passing through the origin (see Figure 3). Output from STRAP are
shown in Appendix B.

This indicates that the independence of the permeability constant
from thickness is valid only for some types of films. Equation 1 states
that the permeability constant (P_r) is a product of its diffusion
coefficient (D) and the solubility (S) in the membrane. It follows that
the independence of the permeability constant from thickness is no longer
true if the film is made from materials that absorb much water, or is
hydrophilic in nature, as demonstrated by the alkyd films which are more
hydrophilic than the epoxy films.

The plots of diffusion rate, R, versus thickness, d, on semi-
logarithmic graph shown in Figure 4 suggest that it is possible that the
diffusion rate of moisture increase inversely in exponential function
with the thickness as the membrane becomes more hydrophilic in nature.

Effect of Vapor Pressure

Equation 2 states that the amount of water (Q) diffusing through
a membrane is directly proportional to the vapor pressure difference
(Δp) and that the permeability constant (P_r) is independent of the
vapor pressure difference (Δp). This linear dependence of (Q) on vapor
pressure difference (Δp) was examined by subjecting two types of 2-mil-
thick unpigmented films (alkyd and epoxy), to a series of different
vapor pressure differences (Δp) at a constant temperature.

The results of the diffusion rates and the permeability constants
are given in Table 5. They show that the diffusion rate of both films
(alkyd and epoxy) increased with vapor pressure difference (see Figure
5).

Here again, as mentioned in the preceeding section, it is not
established that all other generic types of films will behave similarly,
since only two types of clear films (alkyd and epoxy), were tested.
However, it can be reasonably assumed that most other types of paint
films will behave similarly. It would be desirable, if time permits,
to use many other different generic types of films in this type of study
since so many different types of coating have been developed in recent
years.

The average permeability constant (P_r) of the alkyd and epoxy
films were 3.478 ± 0.333 and 1.024 ± 0.110 $\mu g/mm/cm^2/hr/cmHg$ at the
95% confidence limits respectively.

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Examination of Table 5 reveals that the permeability constant of each film, alkyd and epoxy, seems to increase with vapor pressure difference. If permeability constant is independent of vapor pressure change as stated in Equation 2, then a plot of the diffusion rate versus vapor pressure difference would be a straight line passing through the origin with a slop of $(P_r \cdot A)/d$. However, the plot for the alkyd films shows considerable deviation from a straight line, determined by STRAP, as the vapor pressure difference increased, whereas the plot for the epoxy film deviated only slightly. This indicates that the permeability constant of the alkyd film is not independent of vapor pressure difference. The permeability constant of the epoxy film was also affected by vapor pressure difference but to a lesser degree as shown in Figure 5.

A statistical analysis, F-test, was performed to ascertain whether the varying values of the permeability constant were due to the standard deviation of individual measurements or due to the existence of true differences among the permeability constants. For 3 and 16 degrees of freedom, the critical F-value at the 0.01 level was 5.29 for the alkyd, and for the epoxy film for 2 and 12 degrees of freedom, the critical F-value at the 0.01 level was 6.03. The F-ratios obtained, 14.82 and 12.04 for alkyd and epoxy respectively, exceeded their critical values. This indicates that the fluctuations among the permeability constants are not solely due to the standard deviation of individual measurements but due to a true difference among the permeability constants. Hence the permeability constant of both films, alkyd and epoxy, indeed increased as vapor pressure increased.

The deviation from independency of the permeability constant from vapor pressure becomes more apparent with films which are more hydrophilic, as shown by the greater deviation of the alkyd film which is more hydrophilic than the epoxy film. This phenomena may be explained by Equation 1 which states that the permeability constant (P_r) is a product of the diffusion constant (D) and solubility (S), whereas solubility (S) is function of kP as stated in the Equation (6) of Henry's Law.[6,9,23]

$$S = kP \qquad\qquad (6)$$

k is the solubility constant and P is the partial pressure of the penetrant. Thus, if solubility (S) is pressure dependent, then the permeability constant (P_r) will also be pressure dependent as the results of this study appears to corroborate.

Effect of Temperature

The effect of temperature on the diffusion rate and permeability constant of the alkyd and epoxy films, 1.4 and 2.0 mil-thick respectively, were tested by subjecting films to a series of different temperatures while maintaining vapor pressure constant at 30 mmHg. The results are given in Table 6.

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Within the range of temperatures tested, the diffusion rate of the alkyd film appeared unaffected while the epoxy film increased slightly with temperature as shown in Figure 6. The average diffusion rate of alkyd film was 323.29 ± 4.99 $\mu g/cm^2/hr$ at the 95% confidence limits. The coefficient of variation was 5.54% which indicates that the effect of the temperature on the diffusion rate was negligible. The average diffusion rate of the epoxy film, was 47.00 ± 4.56 $\mu g/cm^2/hr$ at the 95% confidence limits. The coefficient of variation was 23.54% which indicates that there is a measurable dependence of diffusion rate on temperature for the epoxy film.

The average permeability constant (P_r) of alkyd film was 4.186 ± 0.142 $\mu g/mm/cm^2/hr/cmHg$ at the 95% confidence limits. The coefficient of variation was 9.02% which indicates that the permeability constant of the alkyd film was independent on the temperature change. The average permeability constant (P_r) of the epoxy film was 1.183 ± 0.115 $\mu g/mm/cm^2/hr/cmHg$ at the 95% confidence limits. The coefficient of variation was 22.87% which indicates a somewhat larger fluctuation of the permeability constant which appeared to increase with an increase in temperature as seen in Table 6.

The results of the above experiments differ from those of other researchers[13,17] who have stated that the increase of permeability as much as doubled for a 10°C rise in temperature. Since the permeability (P_r) is proportional to the product of solubility (S) and diffusion constant (D) as stated earlier in Equation 1, the effect of temperature on permeability is two-fold. The first effect is upon the solubility (S). During the diffusion process, water vapor first condenses on the surface of the membrane as part of the solution process. Since the condensation process of the water vapor is exothermic, the solubility of water into the polymer at the constant vapor pressure decreased as temperature increases. The second effect of temperature is on the diffusion constant (D). Since the diffusion is an activated process,[6,9,13] the diffusion rate of water in the polymer increases as temperature increases. The trend of these two parameters to vary in opposite direction leads to an anomalous and puzzling variation of the permeability with temperature. However, as the temperature is further raised, the rate of increase of the diffusion constant (D) becomes greater than the rate of decrease of solubility (S), and as a result, the permeability begins to increase with increase in temperature as the results of this study appears to corraborate.

CONCLUSION

A method of measuring the permeability constant and the diffusion rate of water vapor through a polymer film, alkyd or epoxy, by the radiochemical method has been elaborated. It demonstrates that the radiochemical method, as compared to the ASTM Standard Method, is very sensitive, rapid, and precise. The diffusion rate, once a steady state

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of flow is attained, can be measured in shorter time intervals (1 ~ 2 hours) over one day whereas the ASTM Standard Method required readings at 24 hour intervals over one week. The sensitivity of the above counting system can be increased to measure down to 1 microgram (1 x 10^{-6} gm), whereas the analytical balance used in the ASTM Standard Method is accurate to 0.2 mg (200 x 10^{-6} gm). Further, the radiochemical method is versatile in the investigation of other important parameters which influence permeability of water vapor. Such versatility is not possessed by other reported radiochemical methods[16,17,18] or by the ASTM Standard Method.

The data presented in this paper are part of a continuing investigation. Only two types of membrane, alkyd and epoxy, were investigated. Therefore, the results obtained here do not represent the behavior of all other types of film; for these others further research is required. However, it has been demonstrated from the limited data that:

1. The rate of the moisture diffusing through a membrane varied inversely with film thickness.

2. The independence of the permeability constant from thickness is valid, but this condition tends to break down if the film is made of a material that absorbs much water or is hydrophilic in nature.

3. The diffusion rate of moisture increases with an increase of vapor pressure differential.

4. The independence of the permeability constant from vapor pressure is not true for all types of film. This deviation becomes more apparent with films which are more hydrophilic.

5. The effect of temperature on the diffusion rate and the permeability constant is anomalous in that in the temperature range of this test (22° ~ 50° C) the expected related rise with temperature was not conclusive. The permeability constant of the less permeable membranes is more sensitive to temperature changes than those of more permeable membranes.

6. Since a straight line passes through the origin, only one experimental point is required to determine the curve of permeability versus thickness (1/d) or permeability versus vapor pressure difference (Δp). However, plots tend to deviate from the expected straight lines as the membranes become more hydrophilic in nature.

FUTURE WORK

To complete this work, effects on the water vapor permeability of

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films of (1) four different pigments, (2) varied pigment concentrations, and (3) water in the liquid form will be investigated.

ACKNOWLEDGEMENT

Table 1. Reliability of Measured Value
Obtained by the Radiochemical Method.[1]

	Counts Per Ten Minutes				
	1	2	3	4	5
Channel (A)	67156	67112	67181	67379	67344
Channel (B)	66271	66703	66565	66988	66724
Total	133427	133905	133746	134367	134069
S. D.[2]	365.27	365.93	365.71	366.56	366.15
Random Error (%)	0.273	0.273	0.273	0.272	0.273
Average Random Error (%)	0.273				

[1] Unpigmented alkyd film, 2.1 mil; vapor pressure, 20 mmHg; temperature, 30°C; exposure time, 123 minutes.

[2] S. D. = Standard Deviation

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Table 2. **Analysis** of Water Vapor Diffusion
Rate Obtained by Radiochemical Method.

Alkyd Film [1] Thickness, mil	0.9	1.9	2.7	3.5
Diffusion Rate, $\mu g/cm^2/hr$	358.30	197.33	151.69	102.58
At 95% Confidence Limits	±17.94	± 6.55	±14.15	± 4.83
Standard Deviation	14.43	5.27	11.38	3.89
Cv, % [2]	4.02	2.67	7.50	3.79

[1] Unpigmented alkyd film (TT-R-266, Type II).

[2] A measure of relative dispersion about the sample mean.

Table 3. Analysis of Water Vapor Diffusion Rate Obtained
by ASTM Standard Method (D1653-62).

Alkyd Film [1] Thickness, mil	0.9	1.9	2.7	3.5
Average Diffusion Rate, $\mu g/cm^2/hr$	380.38	196.32	136.80	132.48
At 95% Confidence Limits	± 41.91	± 20.35	± 14.57	± 98.26
Standard Deviation	33.71	16.37	11.72	79.03
Cv, %	8.86	8.32	8.56	59.66[2]

[1] Unpigmented alkyd film (TT-R-266, Type II).

[2] Did not attain a steady-state of flow for three days.

Table 4. Effect of Thickness on Permeability [1]

Film Thickness, Microns, mils	Diffusion Rate, $\mu g/cm^2/hr$	Permeability Constant, $\mu g/mm/cm^2/hr/cmHg$
Alkyd Film:		
114.3 (4.5)	67.29	3.617
101.6 (4.0)	79.72	3.841
88.9 (3.5)	102.58	5.488
68.5 (2.7)	151.68	5.105
48.2 (1.9)	197.33	4.756
35.5 (1.4)	236.99	4.213
25.4 (1.0)	265.42	3.344
22.8 (0.9)	358.36	4.095
		Ave. 4.196
Epoxy Film:		
101.6 (4.0)	22.68	1.152
50.8 (2.0)	35.89	0.911
25.4 (1.0)	73.73	0.936
		Ave. 1.000

[1] Vapor pressure, 2.0 cmHg; temperature, 30°C.

Table 5. Effect of Vapor Pressure on Permeability [1]

Vapor Pressure, cmHg	Diffusion Rate, $\mu g/cm^2/hr$	Permeability Constant, $\mu g/mm/cm^2/hr/cmHg$
Alkyd Film: (2.0 mil)		
2.0	114.74	2.690
2.5	176.83	3.383
3.0	205.52	3.480
3.5	300.48	4.?61
		Ave. 3.478
Epoxy Film: (2.0 mil)		
2.0	35.89	0.911
3.0	55.42	0.938
4.0	96.32	1.223
		Ave. 1.024

[1] Temperature, 30°C.

Table 6. Effect of Temperature on Permeability [1]

Temperature C^o	Diffusion Rate, $\mu g/cm^2/hr$	Permeability Constant, $\mu g/mm/cm^2/hr/cmHg$
Alkyd Film: (1.4 mil)		
27°C	229.25	4.076
30°C	230.15	4.252
35°C	238.86	4.247
40°C	230.49	4.133
45°C	217.02	3.858
50°C	237.75	4.227
	Ave. 232.29	Ave. 4.186
	Cv,% 5.54	Cv,% 9.02
Epoxy Film: (2.0 mil)		
22°C	39.88	1.136
25°C	42.43	1.078
30°C	35.89	0.938
40°C	54.35	1.313
48°C	52.54	1.464
	Ave. 47.00	Ave. 1.183
	Cv,% 23.54	Cv,% 22.87

[1] Vapor Pressure, 20 mmHg.

Figure 1. Diffusion Cell.
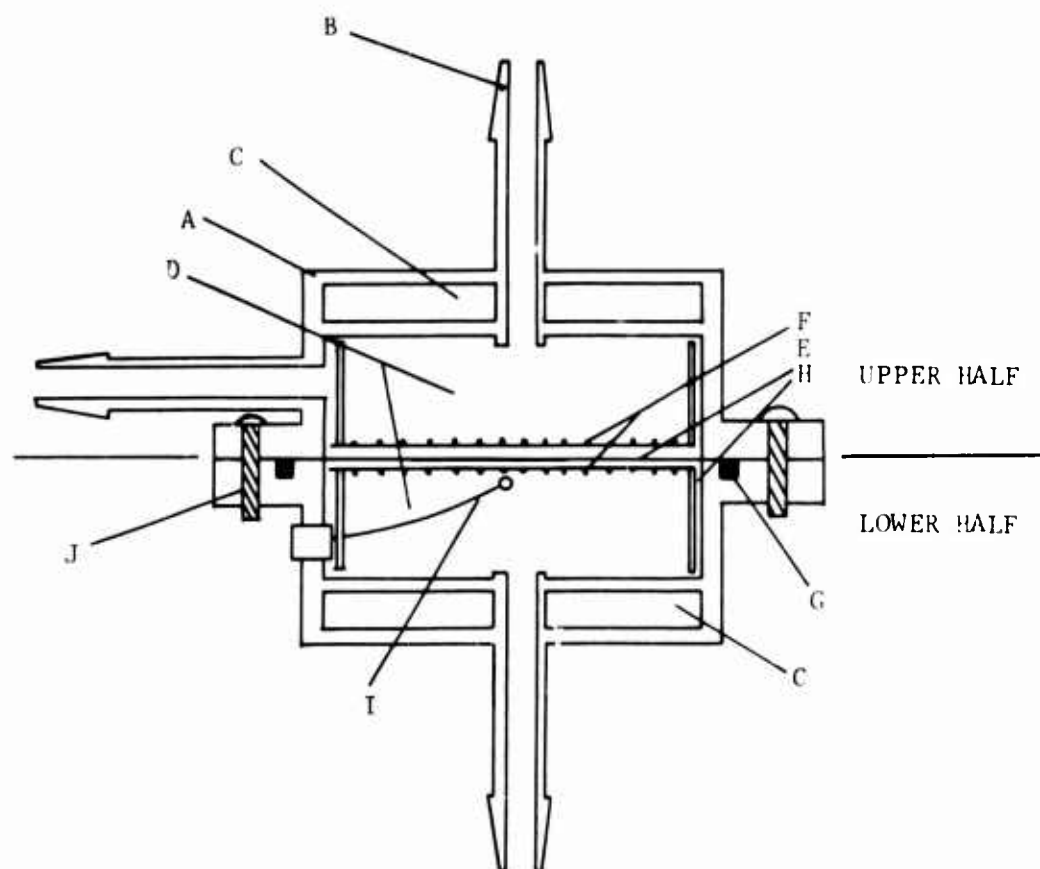
A Plexiglass Wall

B Pyrex Tube

C Water Mantles

D Exposure Chambers

E Sample Membrane

F Copper Gauzes

G O Ring

H Rubber Gasket

I Thermocouple Probe

J Screw

21
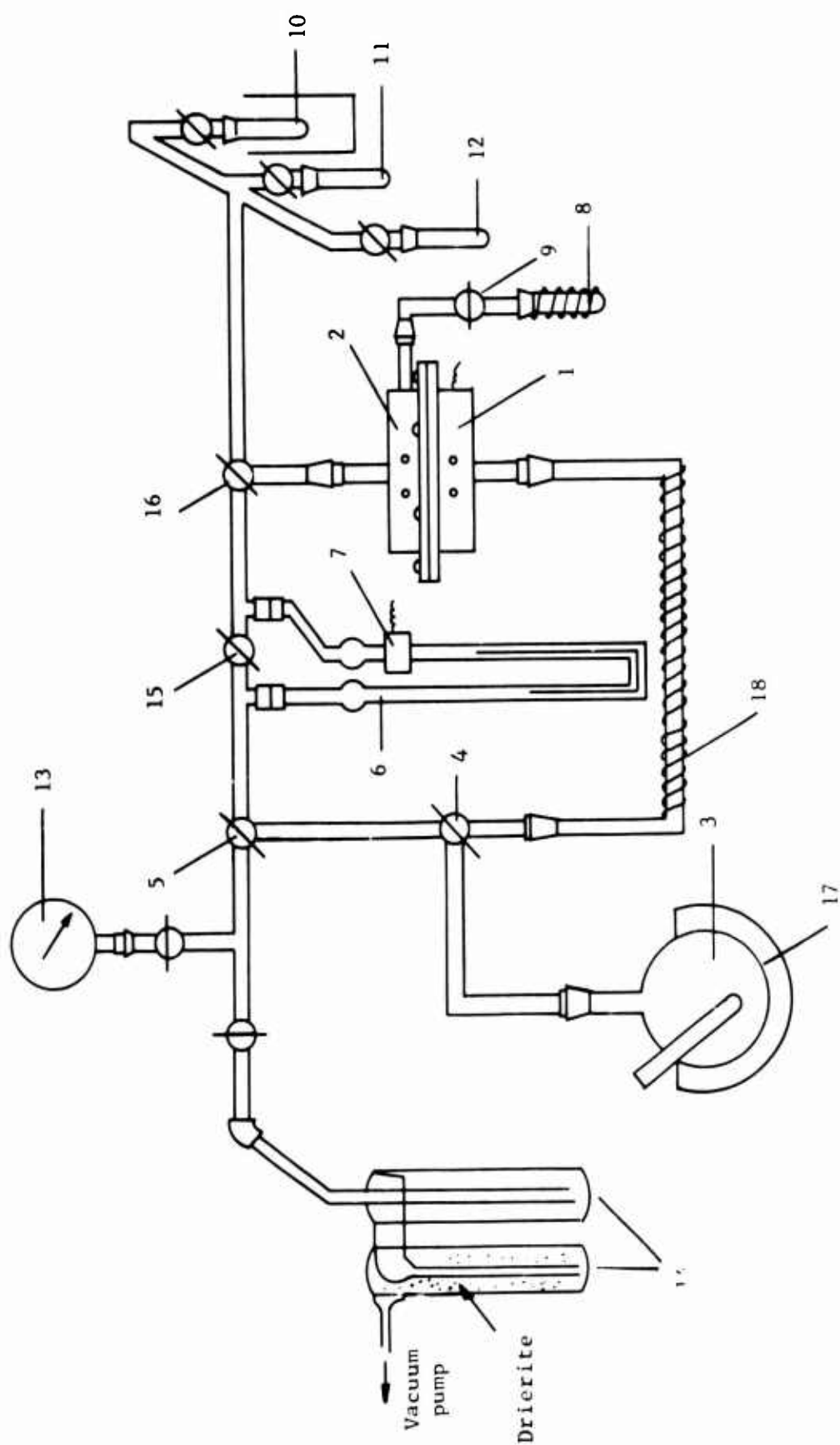
Figure 2. Permeation apparatus for vapor diffusion.

Vacuum pump

Drierite

22
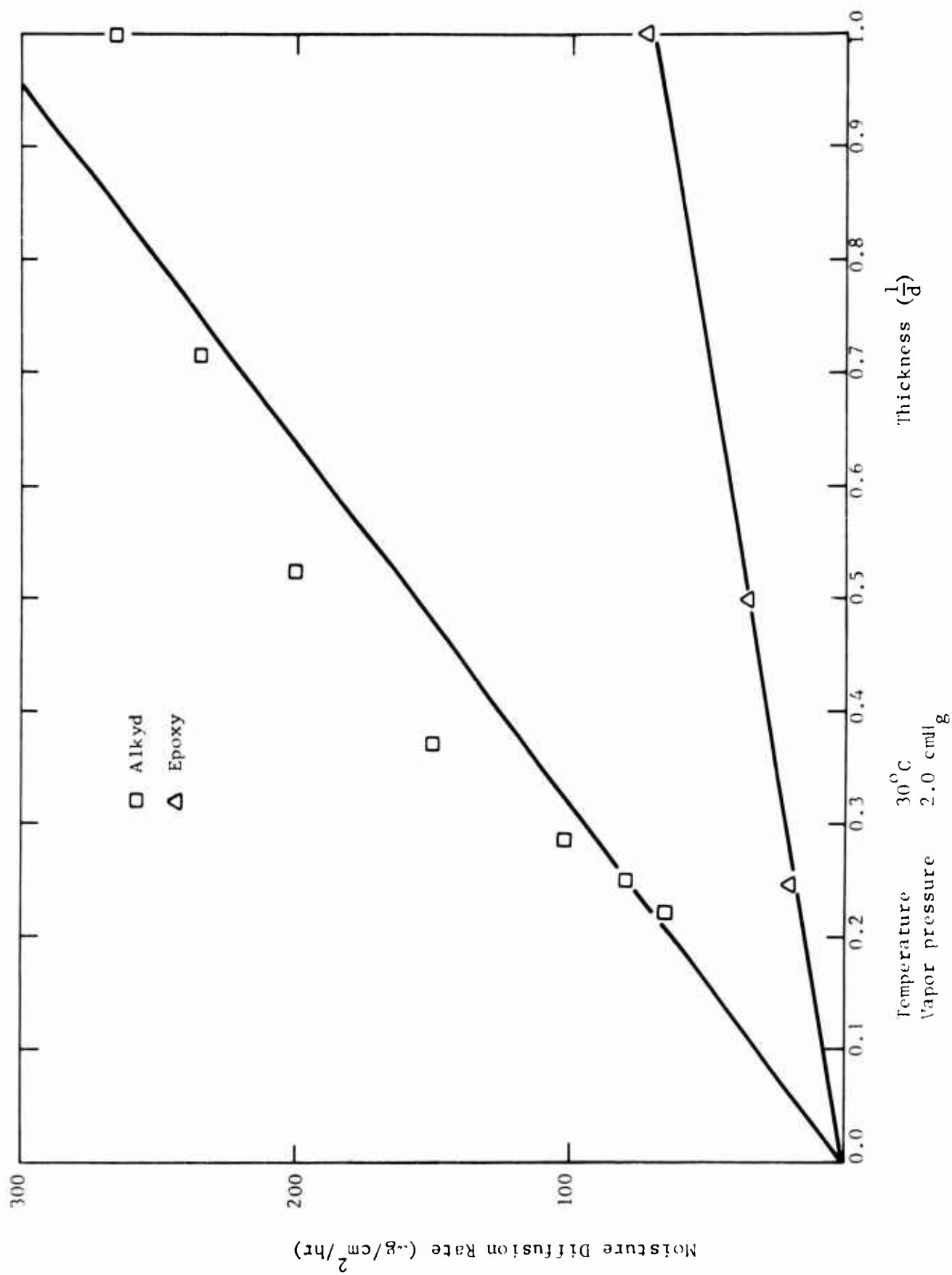
Figure 3. Effect of thickness on permeability.

Temperature 30°C
Vapor pressure 2.0 cmHg

Thickness $(\frac{1}{d})$

Moisture Diffusion Rate ($\mu g/cm^2/hr$)

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Figure 4.   Effect of thickness on permeability.

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Figure 5. Effect of vapor pressure differential on permeability.

25
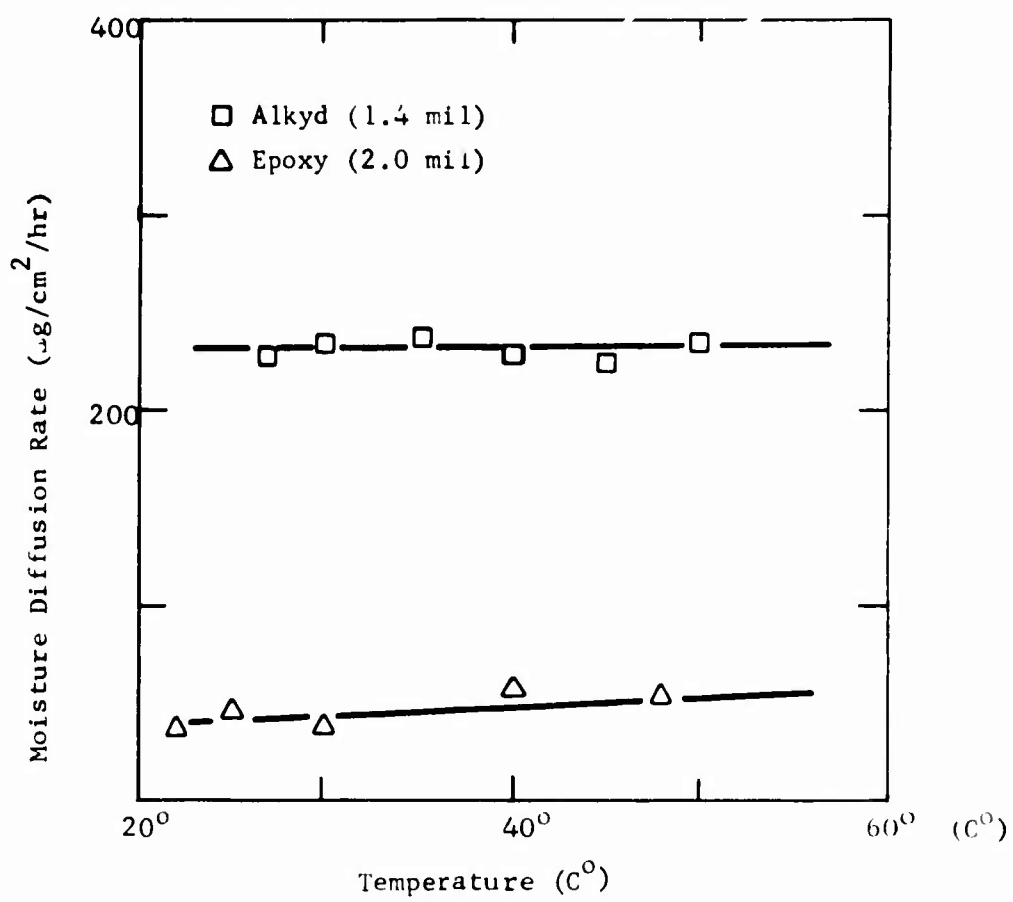
Figure 6. Effect of temperature on permeability.

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APPENDIX A

COMPUTER PROGRAM TO DETERMINE WATER VAPOR PERMEABILITY OF PAINT FILMS

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```
*LDISKWAVPRF
C      WATER VAPOR PERMEABILITY THROUGH PAINT FILMS
       DIMENSION  NO(5),A(5),B(5),TIME(5),T(5),RATIO(5),EFF(5),TOT(5)
       DIMENSION TDH(5),TDHA(5),PERM(5),THICK(5),AREA(5),PRES(5)
       DIMENSION ACTVTY(5),TEMP(5),DA(5),TF(5),S(5),O(5),AB(17)
       READ 500,A1,A2,A3
  500  FORMAT(3E15.8)
  700  READ 900,M,BL
  900  FORMAT(I5,A2)
       IF(M-5)1,1,97
   97  TYPE 709
  709  FORMAT(44HUSE A MAXIMUM OF FIVE DATA CARDS-TRY AGAIN   )
       GO TO 99
    1  DO 11 I=1,M
       READ 901,NO(I),T(I),A(I),B(I),TIME(I),THICK(I),AREA(I),PRES(I),
      1ACTVTY(I),TEMP(I),DA(I),TF(I),S(I),O(I)
  901  FORMAT (I2,F4.2,2F8.2,1X,F5.0,F5.1,2F4.0,F8.0,F4.0,2A4,1X,2A4)
    2  A(I)=A(I)/T(I)
       B(I)=B(I)/T(I)
       TOT(I)= A(I)+B(I)
       RATIO(I) = B(I)/A(I)
       EFF(I)=A1+A2*RATIO(I)+A3*RATIO(I)**2
       TIME(I)= TIME(I)/60.0
       TDH(I)=TOT(I)/(ACTVTY(I)*EFF(I)*TIME(I))*100.
       TDHA(I)=TDH(I)/AREA(I)
       THICK(I)=THICK(I)*.0254
   11  PERM(I)=(THICK(I)*TDHA(I))/PRES(I)
       PUNCH 701
  701  FORMAT(3X,2HNO,7X,4HFILM,8X,4HFILM,3X,4HFILM,4X,5HVAPOR,6X,
      13HT20,9X,4HDATE)
       PUNCH 702
  702  FORMAT(47H               THICKNESS   AREA   TEMP   PRESSURE,12H  AC
      1TIVITY )
       PUNCH 703
  703  FORMAT(39H                (MM)      (CM)2  (C)    ,19H (CMHG)   (C
      1PM/MG)/)
       DO 13 I=1,M
       PUNCH 903,NO(I),THICK(I),AREA(I),TEMP(I),PRES(I),ACTVTY(I),DA(I),T
      1F(I)
  903  FORMAT(3X,I2,8X,F6.4,4X,F5.1,2X,F5.1,4X,F5.1,4X,F9.1,4X,A4,A4)
   13  CONTINUE
       PUNCH 704
  704  FORMAT(// ,79H                               TRIAL      TRIAL       TR
      1IAL      TRIAL     TRIAL)
       PUNCH 705
  705  FORMAT(27X,50H 1            2            3            4           5)
       PUNCH 904,(DA(I),TF(I),I=1,M)
  904  FORMAT(13HSAMPLE NUMBER,7X,5(4X,A4,A4))
       PUNCH 905,(TIME(I),I=1,M)
  905  FORMAT(16HTIME OF EXP(HRS),2X,5F12.3)
       PUNCH 906,(A(I),I=1,M)
  906  FORMAT(14HCHANEL A  (CPM),5X,5F12.1)
       PUNCH 907,(B(I),I=1,M)
  907  FORMAT(14HCHANEL B  (CPM),5X,5F12.1)
       PUNCH 908,(TOT(I),I=1,M)
  908  FORMAT(14HTOTAL N  (CPM),5X,5F12.1)
       PUNCH 909,(RATIO(I),I=1,M)
  909  FORMAT(14HRATIO (B/A)    ,5X,5F12.5)
       PUNCH 910,(EFF(I),I=1,M)
  910  FORMAT(15HEFFICIENCY(O/O),3X,5F12.2)
       PUNCH 911,(TDH(I),I=1,M)
  911  FORMAT(20HT20 DIFFUSED (MG/HR),5F12.5)
       PUNCH 912,(TDHA(I),I=1,M)
  912  FORMAT(9X,11H(MG/HR/CM2),5F12.5)
       PUNCH 913,(PERM(I),I=1,M)
  913  FORMAT(12HPERMEABILITY/1X,8HCONSTANT/1X,19H(MG/HR/CM2/CMHG/MM),5F1
      12.8//)
   99  GO TO 700
       END
```
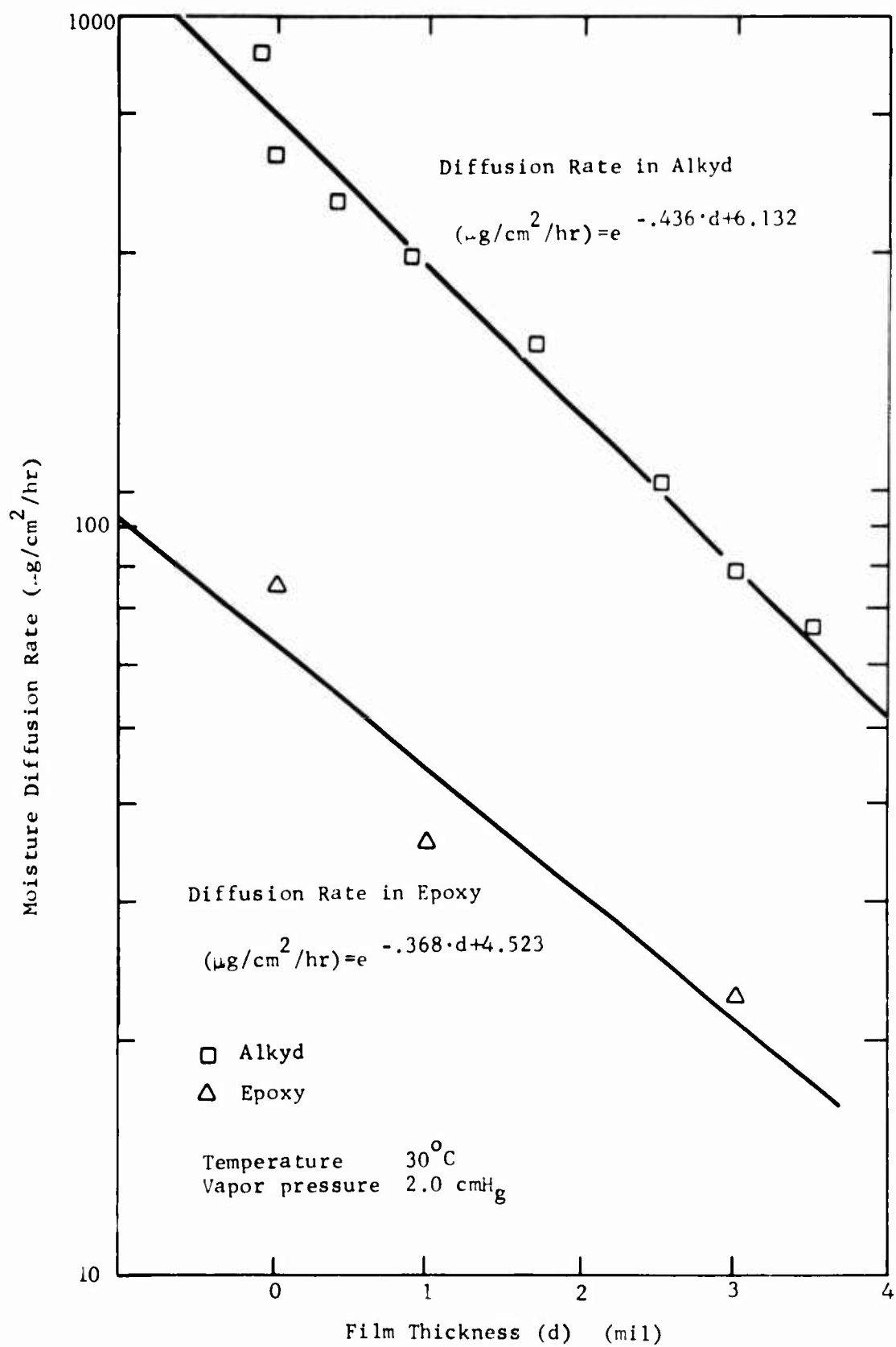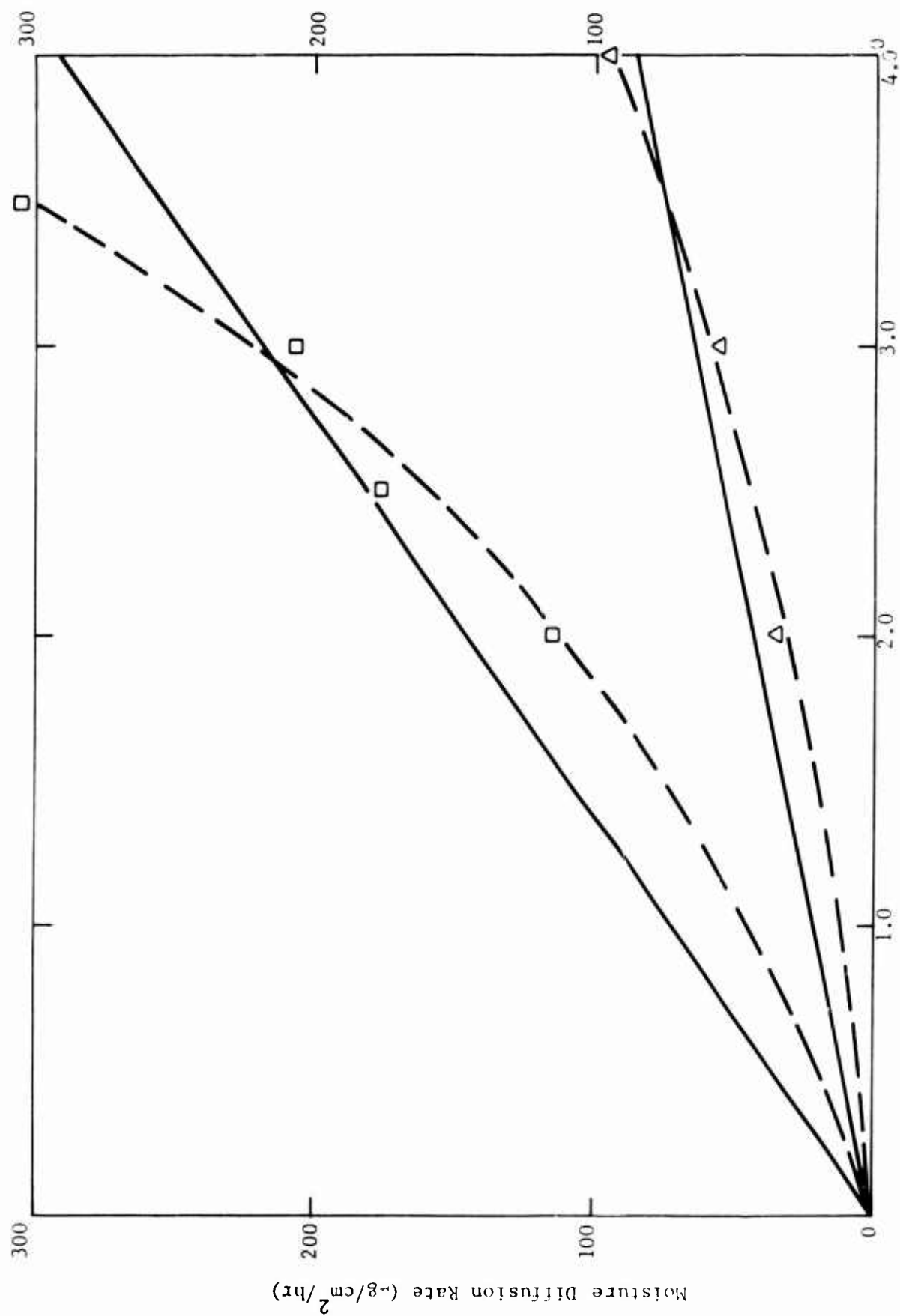
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TABLE A.   SAMPLE INPUT AND OUTPUT DATA OF MOISTURE PERMEABILITY


```
3400032007013600003200702490004651196361130010260024020000
ZZJOB
ZZXEQSWAVPRE
-23.46          51.51          -7.87
     5
211000 8102200 9108300 156. 2.0  20. 4.0 14948.  30. 3=11=68  FPOXY
221000 5050200 5591000 96.  2.0  20. 4.0 14948.  30. 3=11=68  FPOXY
231000116997012799900 186. 2.0  20. 4.0 14948.  30. 3=12=68  FPOXY
241000 5448700 6036600 114. 2.0  20. 4.0 14948.  30. 3=12=68  FPOXY
251000 7676400 8443000 135. 2.0  20. 4.0 14948.  30. 3=12=68  FPOXY
```

NO	FILM THICKNFSS (MM)	FILM AREA (CM)2	FILM TEMP (C)	VAPOR PRESSURF (CMHG)	T2O ACTIVITY (CPM/MG)	DATF
21	.0508	20.0	30.0	4.0	14948.0	3=11=68
22	.0508	20.0	30.0	4.0	14948.0	3=11=68
23	.0508	20.0	30.0	4.0	14948.0	3=12=68
24	.0508	20.0	30.0	4.0	14948.0	3=12=68
25	.0508	20.0	30.0	4.0	14948.0	3=12=68

	TRIAL 1	TRIAL 2	TRIAL 3	TRIAL 4	RIAL 5
SAMPLE NUMBER	3=11=68	3=11=68	3=12=68	3=12=68	3=12=68
TIME OF EXP(HRS)	2.600	1.600	3.100	1.900	2.250
CHANEL A (CPM)	8102.2	5050.2	11699.7	5448.7	7676.4
CHANEL B (CPM)	9108.3	5591.0	12799.9	6036.6	8443.0
TOTAL N (CPM).	17210.5	10641.2	24499.6	11485.3	16119.4
RATIO (B/A)	1.12417	1.10708	1.09403	1.10789	1.09986
EFFICIENCY(0/0)	24.50	23.92	23.47	23.94	23.67
T2O DIFFUSED (MG/HR)	1.80743	1.86004	2.25229	1.68864	2.02449
(MG/HR/CM2)	.09037	.09300	.11261	.08443	.10122
PERMEABILITY CONSTANT (MG/HR/CM2/CMHG/MM)	.00114772	.00118112	.00143020	.00107229	.00128555

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STRAP (STEPWISE LINEAR REGRESSION ANLYSIS PROGRAM) DATA FOR PLOTTING WATER
VAPOR DIFFUSION RATE VS VARIOUS PARAMETERS.

R = DIFFUSION RATE
D = FILM THICKNESS
lNR = NATURAL LOG OF DIFFUSION RATE
ΔP = VAPOR PRESSURE GRADIENT

TABLE B-1. OUTPUT FROM STRAP FOR R VS 1/D PLOTS OF FIG. 3 FOR ALKYD FILMS

NO. OF IND. VARIABLES   01
DEPENDENT VARIABLE NO.   01
NO. OF OBSERVATIONS   040

TOLERANCE LEVEL   .1000000-03

STEP NO.	ENTERING VAR.	ERROR OF EST.	F TO ENTER	F VALUE
01	01	.2871615+02	.1000000-01	.2017832+04

	VARIABLE NO.	COEFFICIENT	ERROR OF COEF.
	01	.3150659+03	.7013889+01

R SQUARE = .9810390+00

STUDENTS T = .2023000+01

NO.	OBSERVED	FITTED	CONFIDENCE LIMITS		RESIDUAL
001	.3566900+03	.3500732+03	.2898792+03	.4102673+03	-.6616760+01
002	.3485200+03	.3500732+03	.2898792+03	.4102673+03	.1553240+01
003	.3756200+03	.3500732+03	.2898792+03	.4102673+03	-.2554676+02
004	.3410100+03	.3500732+03	.2898792+03	.4102673+03	.9063240+01
005	.3699700+03	.3500732+03	.2898792+03	.4102673+03	-.1989676+02
006	.2215200+03	.3150659+03	.2552654+03	.3748664+03	.9354592+02
007	.3007100+03	.3150659+03	.2552654+03	.3748664+03	.1435592+02
008	.2972200+03	.3150659+03	.2552654+03	.3748664+03	.1784592+02
009	.2591300+03	.3150659+03	.2552654+03	.3748664+03	.5593592+02
010	.2485600+03	.3150659+03	.2552654+03	.3748664+03	.6650592+02
011	.2283600+03	.2250471+03	.1660768+03	.2840173+03	-.3312920+01
012	.2455700+03	.2250471+03	.1660768+03	.2840173+03	-.2052292+02
013	.2321100+03	.2250471+03	.1660768+03	.2840173+03	-.7062920+01
014	.2474800+03	.2250471+03	.1660768+03	.2840173+03	-.2243292+02
015	.2314700+03	.2250471+03	.1660768+03	.2840173+03	-.6422920+01
016	.1916400+03	.1658242+03	.1072534+03	.2243950+03	-.2581584+02
017	.1948600+03	.1658242+03	.1072534+03	.2243950+03	-.2903584+02
018	.2056700+03	.1658242+03	.1072534+03	.2243950+03	-.3984584+02
019	.1985100+03	.1658242+03	.1072534+03	.2243950+03	-.3268584+02
020	.1959800+03	.1658242+03	.1072534+03	.2243950+03	-.3015584+02
021	.1354100+03	.1166911+03	.5836110+02	.1750211+03	-.1871892+02
022	.1654600+03	.1166911+03	.5836110+02	.1750211+03	-.4876892+02
023	.1468100+03	.1166911+03	.5836110+02	.1750211+03	-.3011892+02
024	.1578700+03	.1166911+03	.5836110+02	.1750211+03	-.4117892+02
025	.1528800+03	.1166911+03	.5836110+02	.1750211+03	-.3618892+02
026	.1044900+03	.9001883+02	.3178478+02	.1482529+03	-.1447117+02
027	.9738000+02	.9001883+02	.3178478+02	.1482529+03	-.7361168+01
028	.1007200+03	.9001883+02	.3178478+02	.1482529+03	-.1071117+02
029	.1077200+03	.9001883+02	.3178478+02	.1482529+03	-.1770117+02
030	.1026000+03	.9001883+02	.3178478+02	.1482529+03	-.1258117+02
031	.9121000+02	.7876648+02	.2056551+02	.1369674+03	-.1244352+02
032	.7718000+02	.7876648+02	.2056551+02	.1369674+03	.1586480+01
033	.7141000+02	.7876648+02	.2056551+02	.1369674+03	.7356480+01
034	.8093000+02	.7876648+02	.2056551+02	.1369674+03	-.2163520+01
035	.7810000+02	.7876648+02	.2056551+02	.1369674+03	.6664 0+00
036	.7206000+02	.7001465+02	.1183637+02	.1281929+03	-.2045352+01
037	.6170000+02	.7001465+02	.1183637+02	.1281929+03	.8314648+01
038	.5863000+02	.7001465+02	.1183637+02	.1281929+03	.1133465+02
039	.5901000+02	.7001465+02	.1183637+02	.1281929+03	.1100465+02
040	.6509000+02	.7001465+02	.1183637+02	.1281929+03	.4924648+01

TABLE B-2. OUTPUT FROM STRAP FOR R VS 1/D PLOTS OF FIG. 3 FOR EPOXY FILMS

```
NO. OF IND. VARIABLES    01
DEPENDENT VARIABLE NO.   01
NO. OF OBSERVATIONS      015
```

TOLERANCE LEVEL   .1000000-03

STEP NO.	ENTERING VAR.	ERROR OF EST.	F TO ENTER	F VALUE
01	01	.5467792+01	.1000000-01	.1207737+04

	VARIABLE NO.	COEFFICIENT	ERROR OF COEF.	
	01	.7417600+02	.2134407+01	

R SQUARE = .9885410+00

STUDENTS T = .2145000+01

NO.	OBSERVED	FITTED	CONFIDENCE LIMITS		RESIDUAL
001	.7353000+02	.7417600+02	.6158567+02	.8676634+02	.6460040+00
002	.6962000+02	.7417600+02	.6158567+02	.8676634+02	.4556004+01
003	.8125000+02	.7417600+02	.6158567+02	.8676634+02	-.7073996+01
004	.6241000+02	.7417600+02	.6158567+02	.8676634+02	.1176600+02
005	.8188000+02	.7417600+02	.6158567+02	.8676634+02	-.7703996+01
006	.4099000+02	.3708800+02	.2513828+02	.4903772+02	-.3901998+01
007	.3760000+02	.3708800+02	.2513828+02	.4903772+02	-.5119980+00
008	.3315000+02	.3708800+02	.2513828+02	.4903772+02	.3938002+01
009	.3507000+02	.3708800+02	.2513828+02	.4903772+02	.2018002+01
010	.3266000+02	.3708800+02	.2513828+02	.4903772+02	.4428002+01
011	.2174000+02	.1854400+02	.6759872+01	.3032813+02	-.3195999+01
012	.2252000+02	.1854400+02	.6759872+01	.3032813+02	-.3975999+01
013	.2090000+02	.1854400+02	.6759872+01	.3032813+02	-.2355999+01
014	.2480000+02	.1854400+02	.6759872+01	.3032813+02	-.6255999+01
015	.2346000+02	.1854400+02	.6759872+01	.3032813+02	-.4915999+01

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TABLE B-3. OUTPUT FROM STRAP FOR INR VS D PLOTS OF FIG. 4 FOR ALKYD FILMS

```
NO. OF IND. VARIABLES    01
DEPENDENT VARIABLE NO.   01

NO. OF OBSERVATIONS      040
INDEPENDENT VARIABLES              MEAN VALUES        STD. DEVIATION
01                                 .2487500+01        .1321784+01

DEPENDENT VARIABLE
02                                 .5047275+01        .5861959+00
```

CORRELATION COEFFICIENTS

0102 -.9853865+00

TOLERANCE LEVEL   .1000000-03

```
STEP NO.      ENTERING VAR.     ERROR OF EST.     F TO ENTER       F VALUE
  01              01            .1011539+00       .1000000-01     .1271740+04

              VARIABLE NO.      COEFFICIENT       ERROR OF COEF.
                  01           -.4363473+00       .1223582-01
              PURE CONSTANT     .6132688+01       .3438208-01

              R SQUARE = .9709866+00

              STUDENTS T = .2024000+01
```

NO.	OBSERVED	FITTED	CONFIDENCE LIMITS		RESIDUAL
001	.5876867+01	.5739976+01	.5529002+01	.5950950+01	-.1368911+00
002	.5853696+01	.5739976+01	.5529002+01	.5950950+01	-.1137197+00
003	.5928578+01	.5739976+01	.5529002+01	.5950950+01	-.1886020+00
004	.5831912+01	.5739976+01	.5529002+01	.5950950+01	-.9193590-01
005	.5913422+01	.5739976+01	.5529002+01	.5950950+01	-.1734460+00
006	.5400513+01	.5696341+01	.5485814+01	.5906868+01	.2958 +00
007	.5706146+01	.5696341+01	.5485814+01	.5906868+01	-.9805200-02
008	.5694473+01	.5696341+01	.5485814+01	.5906868+01	.1254500-02
009	.5557330+01	.5696341+01	.5485814+01	.5906868+01	.1390113+00
010	.5515684+01	.5696341+01	.5485814+01	.5906868+01	.1806560+00
011	.5430923+01	.5521802+01	.5312781+01	.5730823+01	.9037890-01
012	.5503582+01	.5521802+01	.5312781+01	.5730823+01	.1822020-01
013	.5447211+01	.5521802+01	.5312781+01	.5730823+01	.7459090-01
014	.5511330+01	.5521802+ 1	.5312781+01	.5730823+01	.1047250-01
015	.5444450+01	.5521802+01	.5312781+01	.5730823+01	.7735200-01
016	.5255619+01	.5303629+01	.5095840+01	.5511417+01	.4801000-01
017	.5272281+01	.5303629+01	.5095840+01	.5511417+01	.3134730-01
018	.5326273+01	.5303629+01	.5095840+01	.5511417+01	-.2264430-01
019	.5290839+01	.5303629+01	.5095840+01	.5511417+01	.1278920-01
020	.5278013+01	.5303629+01	.5095840+01	.5511417+01	.2561600-01
021	.4908307+01	.4954551+01	.4747205+01	.5161896+01	.4624350-01
022	.5108729+01	.4954551+01	.4747205+01	.5161896+01	-.1541787+00
023	.4989139+01	.4954551+01	.4747205+01	.5161896+01	-.3458850-01
024	.5061772+01	.4954551+01	.4747205+01	.5161896+01	-.1072212+00
025	.5029653+01	.4954551+01	.4747205+01	.5161896+01	-.7510260-01
026	.4649091+01	.4605473+01	.4396683+01	.4814263+01	-.4351840-01
027	.4578621+01	.4605473+01	.4396683+01	.4814263+01	.2685210-01
028	.4612404+01	.4605473+01	.4396683+01	.4814263+01	-.6970700-02
029	.4679535+01	.4605473+01	.4396683+01	.4814263+01	-.7406230-01
030	.4630838+01	.4605473+01	.4396683+01	.4814263+01	-.2536500-01
031	.4513165+01	.4387299+01	.4176663+01	.4597935+01	-.1258653+00
032	.4346140+01	.4387299+01	.4176663+01	.4597935+01	.4115890-01
033	.4268438+01	.4387299+01	.4176663+01	.4597935+01	.1188613+00
034	.4393585+01	.4387299+01	.4176663+01	.4597935+01	-.6285300-02
035	.4357990+01	.4387299+01	.4176663+01	.4597935-01	.2930920-01
036	.4277491+01	.4169126+01	.3955939+01	.4382312+01	-.1083735+00
037	.4122284+01	.4169126+01	.3955939+01	.4382312+01	.4684170-01
038	.4071247+01	.4169126+01	.3955939+01	.4382312+01	.9787910-01
039	.4077707+01	.4169126+01	.3955939+01	.4382312+01	.9141870-01
040	.4175771+01	.4169126+01	.3955939+01	.4382312+01	-.6645300-02

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TABLE B-4. OUTPUT FROM STRAP FOR R VS ΔP PLOTS OF FIG. 5 FOR ALKYD FILM

```
NO. OF IND. VARIABLES    01
DEPENDENT VARIABLE NO.   01
NO. OF OBSERVATIONS      020
```

TOLERANCE LEVEL   .1000000-03

STEP NO.	ENTERING VAR.	ERROR OF EST.	F TO ENTER	F VALUE
01	01	.3738567+02	.1000000-01	.5977770+03

	VARIABLE NO.	COEFFICIENT	ERROR OF COEF.	
	01	.7283407+02	.2978962+01	

R SQUARE = .9691947+00

STUDENTS T = .2093000+01

NO.	OBSERVED	FITTED	CONFIDENCE LIMITS		RESIDUAL
001	.7609000+02	.1456681+03	.6643253+02	.2249038+03	.6957814+02
002	.1028100+03	.1456681+03	.6643253+02	.2249038+03	.4285814+02
003	.1130800+03	.1456681+03	.6643253+02	.2249038+03	.3258814+02
004	.1218300+03	.1456681+03	.6643253+02	.2249038+03	.2383814+02
005	.1212500+03	.1456681+03	.6643253+02	.2249038+03	.2441814+02
006	.1250400+03	.1820852+03	.1022995+03	.2618708+03	.5704517+02
007	.1762900+03	.1820852+03	.1022995+03	.2618708+03	.5795170+01
008	.1832400+03	.1820852+03	.1022995+03	.2618708+03	-.1154830+01
009	.1737100+03	.1820852+03	.1022995+03	.2618708+03	.8375170+01
010	.1741100+03	.1820852+03	.1022995+03	.2618708+03	.7975170+01
011	.1733900+03	.2185022+03	.1380494+03	.2989550+03	.4511221+02
012	.2163600+03	.2185022+03	.1380494+03	.2989550+03	.2142210+01
013	.2117300+03	.2185022+03	.1380494+03	.2989550+03	.6772710+01
014	.2056500+03	.2185022+03	.1380494+03	.2989550+03	.1285221+02
015	.2134700+03	.2185022+03	.1380494+03	.2989550+03	.5032210+01
016	.2936600+03	.2549192+03	.1736850+03	.3361535+03	-.3874076+02
017	.3077500+03	.2549192+03	.1736850+03	.3361535+03	-.5283076+02
018	.3027600+03	.2549192+03	.1736850+03	.3361535+03	-.4784076+02
019	.2720700+03	.2549192+03	.1736850+03	.3361535+03	-.1715076+02
020	.3261800+03	.2549192+03	.1736850+03	.3361535+03	-.7126076+02

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TABLE B-5. OUTPUT FROM STRAP FOR R VS ΔP PLTS OF FIG. 5 FOR EPOXY FILM

NO. OF IND. VARIABLES   01
DEPENDENT VARIABLE NO.   01
NO. OF OBSERVATIONS   015

TOLERANCE LEVEL   .1000000-03

STEP NO.	ENTERING VAR.	ERROR OF EST.	F TO ENTER	F VALUE
01	01	.1155265+02	.1000000-01	.5019579+03

	VARIABLE NO.	COEFFICIENT	ERROR OF COFF.
	01	.2149469+02	.9593951+00

R SQUARE = .9728661+00

STUDENTS T = .2145000+01

NO.	OBSERVED	FITTED	CONFIDENCE	LIMITS	RESIDUAL
001	.4099000+02	.4298938+02	.1786948+02	.6810928+02	.1999378+01
002	.3760000+02	.4298938+02	.1786948+02	.6810928+02	.5389378+01
003	.3315000+02	.4298938+02	.1786948+02	.6810928+02	.9839378+01
004	.3507000+02	.4298938+02	.1786948+02	.6810928+02	.7919378+01
005	.3266000+02	.4298938+02	.1786948+02	.6810928+02	.1032938+02
006	.6143000+02	.6448407+02	.3894617+02	.9002197+02	.3054067+01
007	.6090000+02	.6448407+02	.3894617+02	.9002197+02	.3584067+01
008	.5611000+02	.6448407+02	.3894617+02	.9002197+02	.8374067+01
009	.5088000+02	.6448407+02	.3894617+02	.9002197+02	.1360407+02
010	.4777000+02	.6448407+02	.3894617+02	.9002197+02	.1671407+02
011	.9037000+02	.8597876+02	.5986690+02	.1120906+03	-.4391244+01
012	.9300000+02	.8597876+02	.5986690+02	.1120906+03	-.7021244+01
013	.1126100+03	.8597876+02	.5986690+02	.1120906+03	-.2663125+02
014	.8443000+02	.8597876+02	.5986690+02	.1120906+03	.1548756+01
015	.1012200+03	.8597876+02	.5986690+02	.1120906+03	-.1524125+02

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13. ABSTRACT

A method of measuring the permeability constant and the diffusion rate of water vapor through a polymer film by the radiochemical method is elaborated. It demonstrates that the radiochemical method, as compared to the ASTM Standard Method, is precise, sensitive and rapid. The radiochemical method is also useful in the investigation of other parameters which influence permeability of water vapor.

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